A Sorbent Regenerator Simulation Model in Copper Oxide Flue Gas Cleanup Processes

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Sorbent regeneration is an important step in copper oxide flue gas cleanup processes because poor regeneration performance could require higher sorbent circulation rate and inventory, resulting in increased process costs. This article describes a countercurrent moving-bed regenerator model using natural gas as the reducing agent. The model incorporates several aspects important for predicting the regenerator performance, such as gas expansion effects, deviation from first-order kinetics with respect to copper sulfate, and mass transfer limitations. The sorbent residence time predicted by this model is in good agreement with data obtained from the life-cycle test system at the Federal Energy Technology Center. The tests conducted include effects of reactor temperature, the methane to copper sulfate feed ratio, and sorbent residence time, on sorbent regeneration. The regenerator modeling also details the impact of gas velocity on the reactor performance.

INTRODUCTION

Copper Oxide Flue Gas Cleanup processes use copper oxide (CuO) supported on alumina spheres for the simultaneous removal of sulfur dioxide (SO_2) and nitrogen oxides (NO_x) from flue gas (Figure 1). These processes are dry and regenerable, and the recovered sulfur can be sold as either sulfuric acid, liquid SO_2, or elemental sulfur, depending on particular applications. Therefore, these processes have an advantage over wet scrubbing processes in that they do not generate solid wastes, a factor that will become increasingly important as landfill costs become more expensive. Another advantage of the copper oxide processes is the simultaneous removal of SO_2 and NO_x. The sorbent absorbs SO_2 and acts as catalyst in reduction reactions for high NO_x removal. Therefore, CuO processes have the potential to offer a more efficient and economical way to reduce both SO_2 and NO_x emissions as compared to other flue gas cleanup processes, which use two separate processes to curtail SO_2 and NO_x. The moving-bed process is capable of simultaneously removing 99% SO_2 and 95% NO_x from coal-fired combustor flue gas.

The Copper Oxide processes have been studied and tested for some time, and previous efforts have mainly focussed on developing and testing the absorption step. Testing of the Fluidized-Bed Copper Oxide Process ranged from laboratory experiments to process-developmental-scale integrated operation [1-3]. The Moving-Bed Copper Oxide Process is currently being tested in the life-cycle test system at the Federal Energy Technology Center (FETC) [4 - 6]. The other important reaction step in these

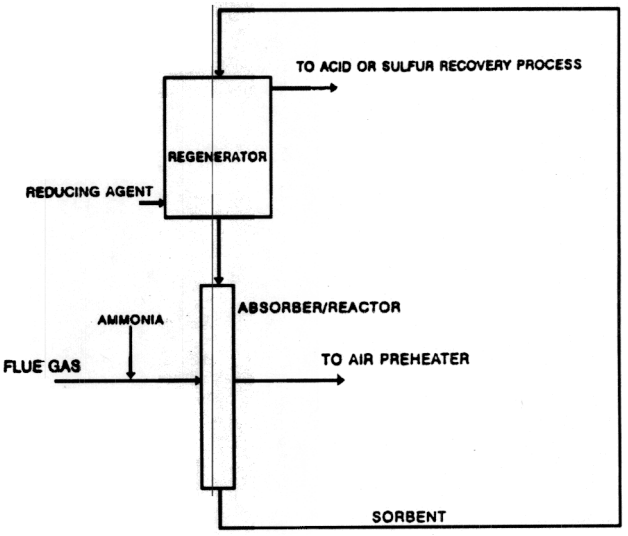

FIGURE 1. Schematic diagram of copper oxide process.

processes is the regenerator. Because the regenerator efficiency will affect the sorbent circulation rate, sorbent inventory requirement, and the associated attrition loss, it will have a significant impact on the overall process cost. For example, in a previous Life-Cycle Test Unit operated at FETC using a fluidized-bed absorber and a continuous countercurrent moving-bed regenerator, only 20%-50% of the spent sorbent fed to the regenerator was reduced at 450°C for a residence time as long as one to two hours. This indicates that sorbent circulation rates are several times higher than the theoretical flow required to achieve the desired SO_2 removal [7]. Thus, for future process development, there is a strong incentive to improve the regeneration efficiency.

Markussen et al., carried out a comprehensive study of sorbent regeneration kinetics using methane as the reducing agent in a microbalance test installation [5]. Their main efforts focused on the impact of various mixtures of reactant and product gases that occur in real regenerators, and a new kinetic equation was established that considers the effects of the concentrations of SO_2 and CH_4 on the reaction kinetics.

In contrast to the microbalance kinetic study where the reagent gas concentrations are well-controlled, the concentrations of reactants and products vary from point to point in a real countercurrent moving-bed regenerator. Additionally, the gas velocity in regenerators may also be different from that in the kinetic study. In order to predict the overall performance, such as estimating the sorbent residence time for a required sorbent regeneration, a regenerator model is required. A model formulation is reported here. It retains the main features of the newly developed kinetics, and that considers the deviations from first-order kinetics with respect to $CuSO_4$ at moderate and high sorbent conversions, the gas expansions, and the slowdown in reaction rate at low gas velocity. The model's predictions are in good agreement with the data obtained in FETC's life-cycle test system. The developed model can be used to provide the information required for plant design and optimization, and will also help in identifying issues that need to be addressed to improve regeneration performance.

BASIC REACTIONS AND MODIFIED REGENERATION KINETICS

In a copper oxide flue gas cleanup process, CuO reacts with SO_2 and oxygen to form copper sulfate ($CuSO_4$). This SO_2-removal reaction occurs in the absorber at approximately 400°C.

$$CuO + SO_2 + 1/2O_2 \rightarrow CuSO_4 \qquad (1)$$

Catalytic reduction of NO_x to nitrogen by ammonia (NH_3) is achieved in the absorber. Both $CuSO_4$ and CuO act as catalysts in the reduction reactions.

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \qquad (2)$$

$$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O \qquad (3)$$

The sulfated sorbent is then regenerated at 450°500°C with methane (in the form of natural gas) in a moving-bed reactor, where the reducing gas flows countercurrent to the downward moving solid sorbent. The overall reduction reaction is

$$CuSO_4 + 1/2CH_4 \rightarrow Cu + SO_2 + 1/2CO_2 + H_2O \qquad (4)$$

Markussen et al., [5] have developed the following kinetic model for the regeneration reaction using the data obtained in a microbalance study and a Langmuir-Hinshelwood mechanism:

$$\frac{dC_A}{dt} = -k_1 C_A \qquad (5)$$

$$k_1 = \frac{k_2 P_{CH_4}}{1 + K_1 P_{CH_4} + K_2 P_{SO_2}} \qquad (6)$$

where C_A = mole concentration of $CuSO_4$,
P_{CH_4}, P_{SO_2} = partial pressures of CH_4 and SO_2 respectively,
K_1, K_2 = the adsorption equilibrium constants for CH_4 and SO_2, respectively,
k_2 = the product of the probability of reaction and the adsorption equilibrium constant for CH_4 (K_1).

This kinetic equation differs from one given previously [7] in that the CO_2 inhibition term has been eliminated because the recent studies [5] have found that the presence of CO_2 in the gas stream has little or no effect on the first-order rate constant [8].

The equation shows a first-order behavior with respect to $CuSO_4$ concentration. The concentration of $CuSO_4$ can be expressed by $C_A = C_{A_0}(1-X_A)$ where C_{A_0} is the molar concentration of $CuSO_4$ at the reactor sorbent inlet, and X_A is the $CuSO_4$ fractional conversion. The kinetic equation in terms of X_A is written as

$$\frac{dX_A}{dt} = k_1(1 - X_A) \qquad (7)$$

with k_1 given by Eq. 6.

Table 1. Values for k_1, k_2, and K_2

Temperature (°C)	K_1 (atm^{-1})	k_2 ($min^{-1}\ atm^{-1}$)	K_2 (atm^{-1})
450	2.07	0.71	8.41
480	1.56	1.38	5.19
510	2.05	2.79	3.00

In Table 1 [6], k_2 k_1 and k_2 are given for three different temperatures.

In this report, two modifications to the regeneration kinetics are introduced: (1) The deviation from the first-order reaction kinetics is considered, (2) Analytic formulas for the temperature dependence of k_2, K_1, and K_2 were established so that the kinetic equation can be applied to different temperatures other than the three temperatures tested in the microbalance study.

regenerator is 15.6 in. and the gas velocity is estimated to be about 0.02 ft/sec.] while the gas velocity in the kinetic study was around 0.7 ft/sec [9]. The low gas velocity in the regenerator will cause a lower partial pressure of natural gas and higher partial pressures of SO_2 and CO_2 on the sorbent surface as compared to those in the bulk phase. These effects can reduce the reaction rate. The microbalance data [8] did show a significant drop in the rate constant (k_1) when the gas flow rate was reduced from 2600 to 1000 sccm (Figure 6). In theory, the pressure difference across the gas film can be estimated through calculations based on engineering correlations [9]. The pressure differences have to be evaluated at each point because they depend on the rate of reaction and the concentrations of all gas species at that point. In this model, we take a more direct approach by introducing an apparent rate constant factor ζ, which is the ratio of observed rate constant to the kinetic rate constant free of mass transfer effects. At 450°C, the data in Figure 6 can be fit with

$$\zeta \approx 1.2\sqrt{\mu_g},$$

for $u_g < 0.7$, where u_g is the gas velocity (ft/sec). For $u_g < 0.7$, we choose ζ=1. The curve shows ζ drops rapidly for small gas velocity, and available data at that region are scarce. The effective rate constant k_{eff} will be the product of k_1 and the apparent rate factor, $k_{eff} = \zeta k_1$. It is interesting to observe that the square root dependence on gas velocity is consistent with the fact that the mass transfer coefficient k_g is approximately proportional to the square root of gas velocity. [The factor for mass transfer, j_D, is defined as

$$jD = \frac{k_g M_m P_{fA}}{G} Sc^{2/3}$$

[9], where k_g is the mass transfer coefficient, M_m is the mean molecular mass, P_{fA} is the film pressure factor, Sc is Schmidt number, G is the superficial mass flow velocity. Engineering correlation for a packed bed of spheres indicates that j_D=1.66 (Re)$^{-0.51}$ [9] where

$$\mathrm{Re} = \frac{d_p G}{\mu}$$

is the Reynolds number, d_p is the particle diameter. This correlation indicates that k_g is approximately proportional to $G^{0.49}$.] At low velocity, the mass transfer resistance becomes a dominant factor, and its effect on the overall rate constant is manifested. Because of the gas expansion effect, the apparent rate factor should vary with height z. Using Eq. (19), we have

$$\zeta = 1.2\sqrt{u_{g_o}\left(1+\varepsilon\frac{\dot{\eta}}{2}\left(X_{A_e}-X_A\right)\right)}$$

where u_{g_o} is the inlet natural gas velocity.

Incorporating the effect of the gas velocity, the residence time is given by the following integral

$$\tau = \int_o^{X_{A_e}} \frac{dX_A}{\left[1.2\sqrt{u_{g_o}\left(1+\varepsilon\frac{\eta}{2}\left(X_A-X_A\right)\right)P_{CH_{4_o}}} \times \left(\alpha+\beta X_A\right)\left(k_2\frac{(1-X_A)}{\mu-\nu X_A}e^{-X_A} - k_3\frac{X_A^2}{1+\varepsilon\frac{\eta}{2}\left(X_{A_e}-X_A\right)}\right)\right]} \quad (24)$$

where α, β, μ and ν are given earlier in the section on simulation of countercurrent moving-bed regenerators.

Using Eq. (24), a required sorbent residence time can be determined for a given sorbent regeneration efficiency. This is a one-dimensional integral that can be easily evaluated. The other properties, such as the off gas composition can be determined by using the mass balance Eq. (15) and (16). For example, the SO_2 and CH_4 flow rates are given by

$$F_{SO_{2_e}} = F_{A_o} X_{A_e}$$

and

$$F_{CH_{4_e}} = F_{CH_{4_o}} - \frac{1}{2} F_{A_o} X_{A_e}$$

COMPARISON WITH LIFE-CYCLE TESTS

FETC's life-cycle tests have generated a significant amount of useful data on the Copper Oxide Flue Gas Cleanup Processes. Parametric studies with the regenerator have been conducted by varying the sorbent residence time, the methane to sulfur ratio, and the reactor temperature. Results provide valuable information for the simulation model and guidance for designing scale-up systems. The sorbent regeneration efficiency in the regenerator is calculated by analyzing sorbent sulfur content at the inlet and the outlet of the regenerator (or at inlet and outlet of the absorber) during steady-state conditions. Regeneration efficiency is defined as $(S_{in} - S_{out})/S_{in}$ x 100% where S_{in} is wt.% sulfur in sorbent at inlet to the regenerator and S_{out} is wt.% sulfur in sorbent at outlet of the regenerator. It is noted that a certain amount of sulfur is fixed with the sorbent substrate and cannot be regenerated, as the reaction between the SO_2 and the alumina has been documented by several researchers [10,11]. Tests conducted at FETC indicated that the lowest residual sulfur content of the regenerated sorbent is 0.6% by weight for the sorbent used in tests reported here, and this amount of sulfur is believed to be fixed with the substrate. The measured sulfur content minus 0.6% gives the unregenerated sulfur content. The comparisons of predicted sorbent regeneration efficiencies versus experimental data findings are summarized in Table 2.

Table 2. Regenerator Parametric Test Conditions

Test	MBCUO-4						MBCUO-5	
	1	2	3	4	7	8	1	2
Flue gas, scfm	110.7	111	110.9	110.5	112.4	112.4	111	107
Regenerator, temp, °F	839	851	845	850	876	815	857	851
Natural gas flow, lb/h	0.6	0.45	0.3	0.6	0.6	0.6	0.6	0.6
Residence time, min	180	180	180	120	60	60	120	120
Sorbent flow, lb/min	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
Natural gas/sulfur ratio	1.17	0.873	0.59	1.18	1.17	1.17	1.18	1.2
Sulfur content in, wt. %	1.9	2.76	2.83	2.37	2.11	2.56	2.83	2.12
Sulfur content out, wt. %	0.74	0.91	1.15	0.93	1.02	1.47	1.13	1.01
Regeneration Eff. % (experimental)	89	86	75	81	72	56	76	73
Regeneration Eff. % (model) See figures 7, 8, 9 and 10	87.6	79.5	64	80	76	52	80	82

Residence Time Effect

Figure 7 graphs the sorbent regeneration efficiency versus the sorbent residence time at 850°F (454°C) (MBCUO-4-7, MBCUO-4-4, and MBCUO-4-1). The solid curve is the model prediction by Eq. (24). The dash line in the figure is a calculation without considering the mass transfer resistance [Eq. (23)]. It can be seen that the mass film resistance effect is very important in modeling the regenerator, and without the correction for this effect, the predicted required residence time for a given sorbent regeneration would be dramatically underestimated. For example, in a report by A. E. Roberts & Associates, Inc. the estimated residence time for 80% regeneration was estimated at 24 minutes [12], which is very similar to the case the dash line represents.

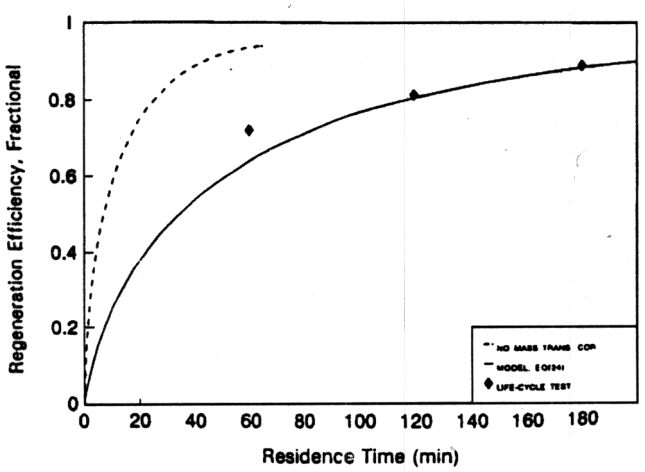

FIGURE 7. Sorbent conversion at different resident times.

Methane to Sulfur Ratio

A change in the methane-to-sulfur feed ratio will change the degree of sorbent regeneration for a given residence time. The reaction stoichiometry indicates the methane-to-sulfur molar ratio should be 0.5. There will be inadequacy of reducing agent for complete sorbent regeneration if the molar ratio is less than 0.5. Increasing the methane supply (lowering η, the inverse of the methane-to-sulfur ratio) will accelerate the sorbent regeneration, as the methane partial pressure will be increased inside the regenerator. The high methane-to-sulfur ratio, however, will increase the consumption of methane and also leave residual methane in the off-gas stream. These factors should be considered in plant design together with the byproduct production using the off-gas stream. For the design of a regenerator, the focus is determining the sorbent conversion for a given methane-to-sulfur ratio and a given sorbent residence time. Three tests, MBCUO-4-1, MBCUO-4-2, and MBCUO-4-3, were dedicated for that purpose. Assuming that the natural gas was 100% methane, the natural gas to sulfur-molar ratios were 1.17, 0.873 and 0.59, and the regenerator operated near 850°F (454°C). The model predictions for three cases were plotted at the dashed, solid, and dotted lines separately. Two factors need to be considered in using Eq. (24) to predict the residence time. First, the actual methane content in the feed natural gas is close to 90%. Second, a portion of methane was reacted by residual

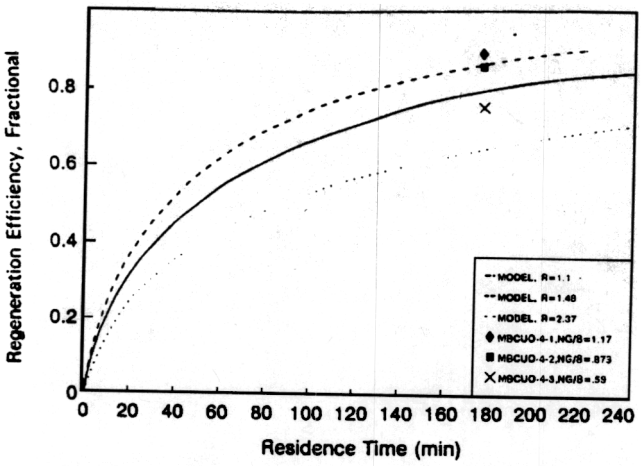

FIGURE 8. Sorbent regeneration at different methane feed rates.

CuO in the sorbent as discussed before. After these adjustments, the estimated sulfur-to-methane molar ratios for the three cases were 1.1, 1.49 and 2.37.

The model closely agrees with the test data. From these curves and data plotted in Figure 8, it can be seen that a surplus of methane above the stoichiometry requirement will improve the sorbent regeneration efficiency. It is interesting to note that when the methane-to-sulfur ratio approaches infinity, the current simulation model (Eq. 24) will be reduced to the case for a kinetic study using a microbalance apparatus.

Temperature Effect

Tests were conducted at two different levels of regeneration temperature to evaluate temperature effect on sorbent regeneration efficiency at 60 minutes sorbent residence time in the regenerator. The sorbent regeneration efficiencies were 56 % and 72 % at regeneration temperatures of 815°F (435°C) and 876°F (469°C) respectively. The model gives a similar prediction. The model prediction and test data comparison is plotted in Figure 9. The dashed line is the calculated result for 876°F (469°C), and the solid line is the calculated result for 815°F (435°C). The dotted line represents model prediction for sorbent regeneration efficiency if the regenerator is operated at 750°F (399°C) at various sorbent residence times in the regenerator. It is seen that the temperature greatly affects sorbent regeneration.

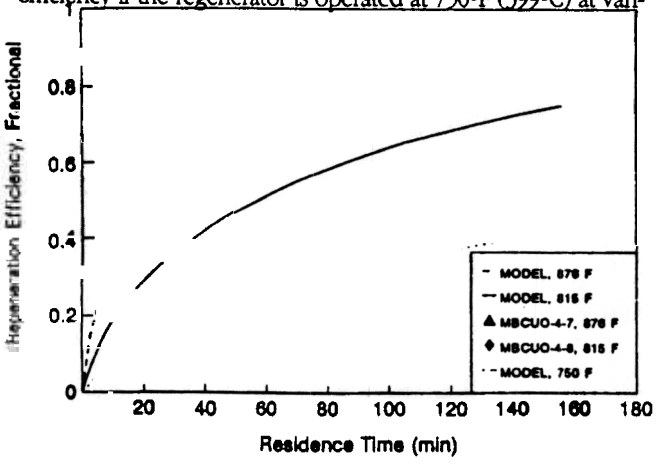

FIGURE 9. Sorbent regeneration at different temperature.

Nitrogen Dilution

In one case, nitrogen was added to the reducing gas into the regenerator. Nitrogen would not likely be used in real applications, but the tests provide another opportunity to verify the simulation model. MBCUO-5-1 and MBCUO-5-2 were both operated at near 850°F (454°C) and 120 minutes residence time. In MBCUO-5- 1 natural gas was fed to the regenerator, and in MBCUO-5-2 the natural gas was diluted by an amount of nitrogen that was equivalent to 50% dilution of the regenerator gas.

Adding nitrogen increases the gas velocity and thus reduces the gas film resistance, and this effect will increase the reaction rate. On the other hand, the dilution with nitrogen reduces the partial pressure in the feed stream, which will slow the reaction. These two factors are competing with each other and the measured sorbent regeneration for 120 minutes residence time are very close as shown in Figure 10. The model predictions for these cases have shown minimal effect of nitrogen dilution. Figure 10 also shows good agreement between model prediction and experimental data on sorbent regeneration efficiency.

CONCLUSIONS

A regenerator mathematical simulation model has been formulated. This simulation model uses a modified regeneration kinetics model, which was also formulated in this study, as the simulation model's basic building block. This simulation model has incorporated mass film resistance effects into its formulation. The regenerator simulation model compared favorably with experimental data gained in life-cycle tests. The model, which can predict the regenerator performance at a different temperature, different methane-to-sulfur ratio, different partial methane pressure, and different gas velocity, will be a useful tool for sensitivity studies and optimum performance searches. From the model calculations confirmed by actual data from the life-cycle tests, it is observed that the sorbent can be regenerated by setting the regenerator temperature at around 850°F (454°C), and

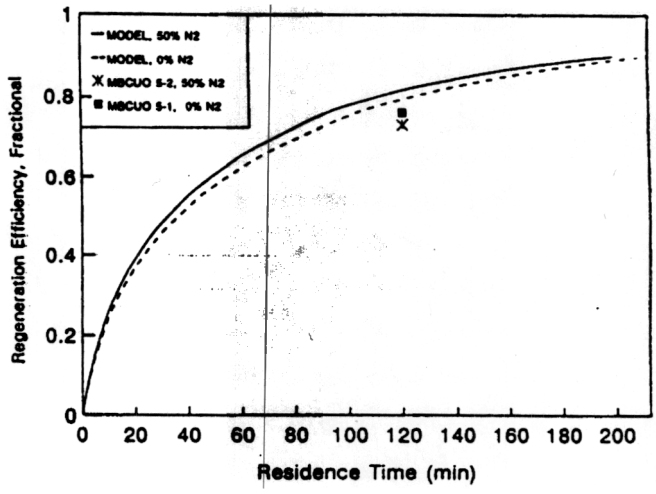

FIGURE 10. Effect of nitrogen dilution.

two to three hours of residence time will be appropriate for about 80% sorbent regeneration efficiency. These calculations and tests show that natural gas is a good agent for sorbent regeneration in CuO processes, and a continuing SO_2 absorption and sorbent regeneration can be realized in the present FETC process configuration.

DISCLAIMER

Reference in this paper to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

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Data by Markussen et al., [5] indicated that the kinetic equation (7) is only applicable in the initial stages of regeneration; when the sorbent fractional conversion exceeds 0.6 to 0.7, the deviation from first-order behavior becomes significant. There also exists an apparent equilibrium limit for sorbent regeneration. This limit implies the existence of reverse reactions and diffusion effects, and to account for this behavior the kinetic equation (7) might be revised to the form of

$$\frac{dX_A}{dt} = k_1(1 - X_A) - k_3 X_A^{\beta} \qquad (8)$$

The second term gives the contribution of the reverse reaction whose rate depends on the concentrations of the products, which, in turn, are proportional to the conversion X_A. The situation is more complicated because the reverse reaction occurs on the surface, and gas absorption and desorption play certain roles in affecting the reaction rate. For the purpose of modeling the regenerator, the main goal is to find a kinetic equation that better represents the available data for the entire range of sorbent conversion, and at the same time is consistent with the findings for small X_A. In examining the curves in reference [5] at 450°C, it is found that

$$\frac{dX_A}{dt} = k_1(1 - X_A)e^{-X_A} - k_3 X_A^2$$

appears to fit the microbalance data quite well [8]. This equation approaches a first-order behavior for small X_A as given by reference [6], and the rate constant k_1 still considers the effects of surface absorption as described by the Langmuir-Hinshelwood mechanism. The added exponential form in the first term is used to help fit the data for intermediate X_A, where pore diffusion effects may play a role in slowing down the reaction rate. The new kinetic equation used for modeling the reactor takes the form

$$\frac{dX_A}{dt} = \frac{k_2 P_{CH_4}}{1 + K_1 P_{CH_4} + K_2 P_{SO_2}}(1 - X_A)e^{-X_A} - k_3 / P_{CH_4} X_A^{\,2} \qquad (9)$$

This kinetic equation will give lower equilibrium limits when SO_2 is present in the gas stream, as observed in the kinetic study. Therefore, this form gives a better prediction than a simple adjustment, which has a fixed equilibrium limit such as using

$$\frac{dX_A}{dt} = k_1\left(X_{A_{eq}} - X_A\right).$$

The observed equilibrium limits [8], $X_{A_{eq}}$ are 0.95 at 450°C, 0.857 at 480°C, and 0.773 at 510°C for 100% CH_4 in the feed gas. k_3' is determined by the equilibrium limits, using

$$\frac{dX_A}{dt} = 0, \text{at } P_{SO_2}$$

approaches zero, and P_{CH_4} approaches 1 yields

$$k_3' = \frac{k_2\left(1 - X_{A_{eq}}\right)e^{-X_{A_{eq}}}}{(1 + K_1)X_{A_{eq}}^2}$$

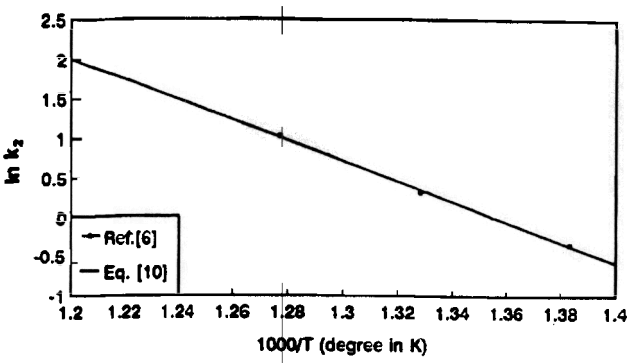

FIGURE 2. Temperature dependence of rate constant k_2.

The second modification introduced is the inclusion of the temperature dependence of the rate constants. Plotting k_2, K_1, and K_2 against 1/T (Figures 2 to 4) it can be found that they can fit well with the following formulas:

$$k_2 = \exp\left(17.485 - \frac{107.258\,\frac{Jole}{mole}}{RT}\right), \min^{-1} atm^{-1}$$

$$K_2 = \exp\left(-11.287 + \frac{80.752\,\frac{Jole}{mole}}{RT}\right), atm^{-1}$$

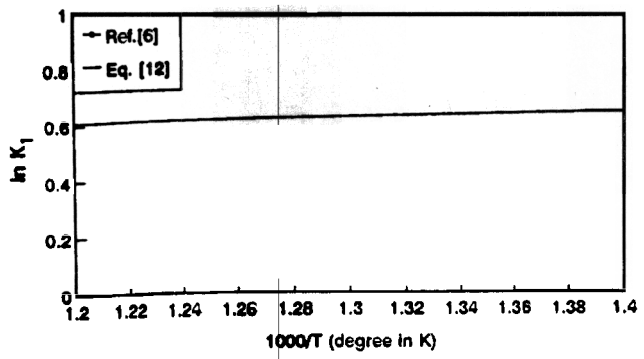

FIGURE 3. Temperature dependence of rate constant, k_2.

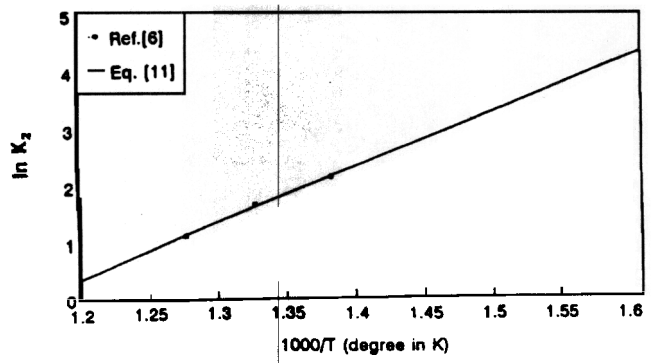

FIGURE 4. Temperature dependence of the equilibrium constant of SO_2.

$$K_1 = \exp\left[0.416 + \frac{1.340\frac{Jole}{mole}}{RT}\right] .atm \qquad (12)$$

The equilibrium limits for different temperatures are interpolated for temperature between 450°C to 480°C and for 480°C to 510°C. For temperatures below 450°C, we assume that the equilibrium limit equals the value at 450°C, which is 0.95. For temperatures above 510°C, the equilibrium limit is assumed to equal the value at 510°C, which is 0.773.

With these modifications we have a kinetic model that predicts the reaction rates for various temperatures.

SIMULATION OF COUNTERCURRENT MOVING-BED REGENERATORS

In a countercurrent moving-bed regenerator, the sorbent moves downward in packed granular form, and the reducing gas CH_4 enters from the bottom of the reactor and leaves at the top. Assuming that the sorbent and the gas phase both move in plug flow, we can express the kinetics at steady-state by the following form:

$$u\frac{dX_A}{dz} = \frac{-k_2 P_{CH_4}(1 - X_A)e^{-X_A}}{1 + K_1 P_{CH_4} + K_2 P_{SO_2}} + k'_3 P_{CH_4} X_A^2 \qquad (13)$$

where z is the vertical coordinate and u is the sorbent velocity (Figure 5).

Replacing the partial pressure with the mole concentration, we have

$$\frac{dX_A}{dz} = \frac{-k_2 C_{CH_4} RT(1 - X_A)e^{-X_A}}{u\left(1 + K_1 C_{CH_4} RT + K_2 C_{SO_2} RT\right)} + \frac{k'_3}{u} C_{CH_4} RTX_A^2 \qquad (14)$$

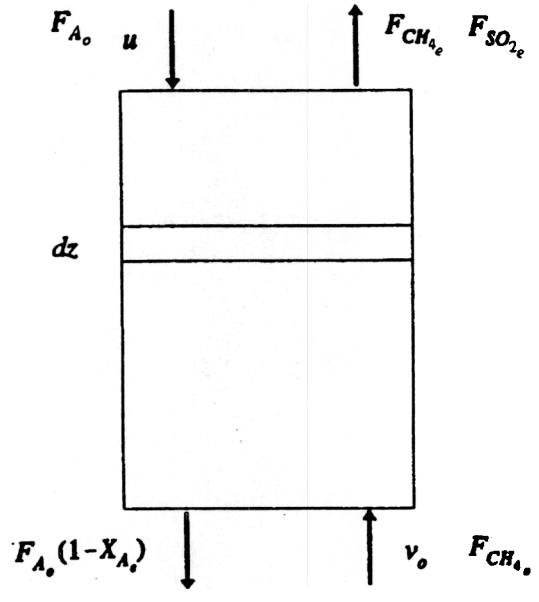

FIGURE 5. Flows in a counterflow moving-bed regenerator.

where R is the molar gas constant, T is the temperature of the reactor (°K), and C_{CH_4}, C_{SO_2} are the molar concentrations of CH_4 and SO_2 respectively.

Different from the tests using the microbalance where the oversupply of methane keeps its concentration constant and changes in the concentrations of C_{CH_4} and C_{SO_2} are negligible, the concentrations of CH_4 and SO_2 vary at each different location in an actual regenerator. A key element in deriving a model for the regenerator is to determine the relationship between the concentrations of CH_4 and SO_2, and the sorbent conversion X_A at each point in the reactor. This can be achieved by examining the material balance and the expansion in gas volume as the reaction proceeds. Since there is no accumulation of materials in a given section between the reactor bottom and a cross-section at z in steady-state (Figure 5), the difference between the flow rates at both ends of the section for each species must equal the amount consumed or generated by the reaction inside the section per unit of time. From the reaction stoichiometry, we can further relate the amount of each species consumed or generated in the section to the amount of sorbent regenerated in the section. Therefore,

$$F_{CH_{4o}} - F_{CH_4} = \frac{1}{2}F_{A_c}\left(X_{A_e} - X_A\right) \qquad (15)$$

$$F_{SO_2} - F_{SO_{2_o}} = F_{SO_2} = F_{A_o}\left(X_{A_e} - X_A\right) \qquad (16)$$

where F_A, F_{CH_4}, and F_{SO_2} are the molar flow rates for $CuSO_4$, CH_4, nd SO_2, respectively, and the subscripts $_{o,e}$ denote the entry and exit conditions for the species of interest. It must be noted that CH_4 and $CuSO_4$ enter the reactor at opposite ends. In a steady-state plug flow, X_A can also be written in terms of F_A, such that

$$X_A = \frac{F_{A_o} - F_A}{F_{A_o}}$$

Because the reaction generates more moles of gases than it consumes, the gas volume increases from the bottom of the reactor to the top. We assume that the volumetric flow rate V of all gases increases linearly with the conversion of methane, and this leads to

$$V = V_o\left(1 + \varepsilon X_{CH_4}\right) \qquad (17)$$

where V_o is the volumetric gas flow rate at the bottom of the reactor, and e is the expansion ratio. Note the conversion of methane is defined as

$$X_{CH_4} = 1 - \frac{F_{CH_4}}{F_{CH_{4o}}}$$

The stoichiometry of the reduction reaction [Eq. (4)] shows that the consumption of one mole of methane will generate five moles of gases. For the isothermal case, the expansion ratio ε equals four. Here, we have neglected the pressure drop in the reactor due to the very low gas flow rate.

X_{CH_4} can be expressed in terms of the fractional conversion of sorbent through a mass balance [Eq. (15)]:

$$X_{CH_4} = \frac{F_{A_o}}{2F_{CH_4 o}}\left(X_{A_e} - X_A\right) = \frac{\eta}{2}\left(X_{A_e} - X_A\right) \qquad (18)$$

where

$$\eta = \frac{F_{A_o}}{F_{CH_{4_o}}}$$

is the molar flow ratio of $CuSO_4$. Caution should be used in calculating η for real regenerators, since it must be noted that some of the natural gas is used in reacting with species other than $CuSO_4$. For example, when the sorbent is introduced into the regenerator, it contains some unreacted CuO. Since CuO reacts with methane at a rate that is faster than $CuSO_4$ [2], the portion available for reducing $CuSO_4$ is less than the nominal feed. Also, it should be noted that natural gas is not 100% methane in a commercial setting. Thus, the volumetric gas flow rate is a function of sorbent conversion X_A,

$$V = V_o\left(1 + \varepsilon\frac{\eta}{2}\left(X_{A_e} - X_A\right)\right) \qquad (19)$$

The concentrations of CH_4 and SO_2 at any point inside the regenerator can be expressed as functions of sorbent conversion X_A at that point,

$$C_{CH_4} = \frac{F_{CH_4}}{V} = \frac{F_{CH_{4_o}} - \frac{1}{2}F_{A_o}\left(X_{A_e} - X_A\right)}{V_o\left(1 + \varepsilon\frac{\eta}{2}\left(X_{A_e} - X_A\right)\right)} \qquad (20)$$

$$C_{SO_2} = \frac{F_{SO_2}}{V} = \frac{F_{A_o}\left(X_{A_e} - X_A\right)}{V_o\left(1 + \varepsilon\frac{\eta}{2}\left(X_{A_e} - X_A\right)\right)}$$

Inserting Eqs. (20) and (21) into Eq. (14)and using

$$\frac{F_{CH_{4_o}}RT}{V_o} = P_{CH_{4_o}},$$

where $P_{CH_{4_o}}$ is the pressure of natural gas entering the regenerator, we obtain

$$\frac{dX_A}{dz} = \frac{-k_2}{u}P_{CH_{4_o}}\left(1 - X_A\right)\frac{\alpha + \beta X_A}{\mu - \nu X_A}e^{-X_A} + \frac{k_3'}{u}P_{CH_{4_o}}\frac{\alpha + \beta X_{A_e}}{1 + \varepsilon\frac{\eta}{2}\left(X_{A_e} - X_A\right)}X_A^2 \qquad (22)$$

where

$$\alpha = 1 - \frac{\eta}{2}X_{A_e},$$

$$\beta = \frac{\eta}{2},$$

$$\mu = \left(1 + \varepsilon\frac{\eta}{2}X_{A_e}\right) + K_1P_{CH_{4_o}}\left(1 - \frac{\eta}{2}X_{A_e}\right) + K_2P_{CH_{4_o}}\eta X_{A_e},$$

$$\nu = \eta\left(\frac{\varepsilon}{2} + K_2P_{CH_{4_o}} - \frac{1}{2}K_1P_{CH_{4_o}}\right)$$

Integrating Eq. (22) over the height of the reactor H. we obtain the sorbent residence time,

$$\tau = \frac{H}{u}$$

as a function of the overall sorbent conversion X_{A_e}.

$$\tau = \int_o^{X_{A_e}} \frac{dX_A}{P_{CH_{4_o}}\left(\alpha + \beta X_A\right)\left[k_2\frac{\left(1 - X_A\right)e^{-X_A}}{\left(\mu - \nu X_A\right)} + k_3'\frac{X_A^2}{1 + \varepsilon\frac{\eta}{2}\left(X_{A_e} - X_A\right)}\right]} \qquad (23)$$

CORRECTION FOR MASS TRANSFER RESISTANCE

Eq.(23) may underestimate the required residence time because it neglects the effect of external mass transfer resistance. This effect should be considered when the actual gas velocity differs from that on which the kinetics is based. This effect is especially important for the sorbent regenerator because of the slow gas velocity used in the regenerator. It is very important to note that since the sorbent carries less than 10% copper by weight, the $CuSO_4$ content in the used sorbent is small. Therefore, it only needs a small amount of methane to react with the sorbent, and the gas velocity could be much smaller than the gas velocity used in kinetics study. A simple calculation indicates that the inlet gas velocity of the regenerator used in FETC's current life-cycle test system is about 0.02 ft/sec (based on void volume) for a molar feed ratio of unity (η=1), [It is estimated that the flow of natural gas is about 0.27 scfm. The internal diameter of the

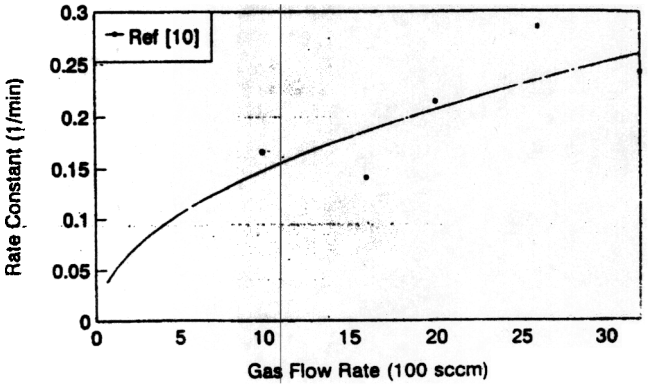

FIGURE 6. Rate Constant vs. gas flow rate in microbalance test.